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Patentanmeldung Nr. Patent application No. Demande de brevet n°

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UCB S.A.

Allée de la Recherche 60

1070 Bruxelles

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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:

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Process using a cyclic carbonate reactant

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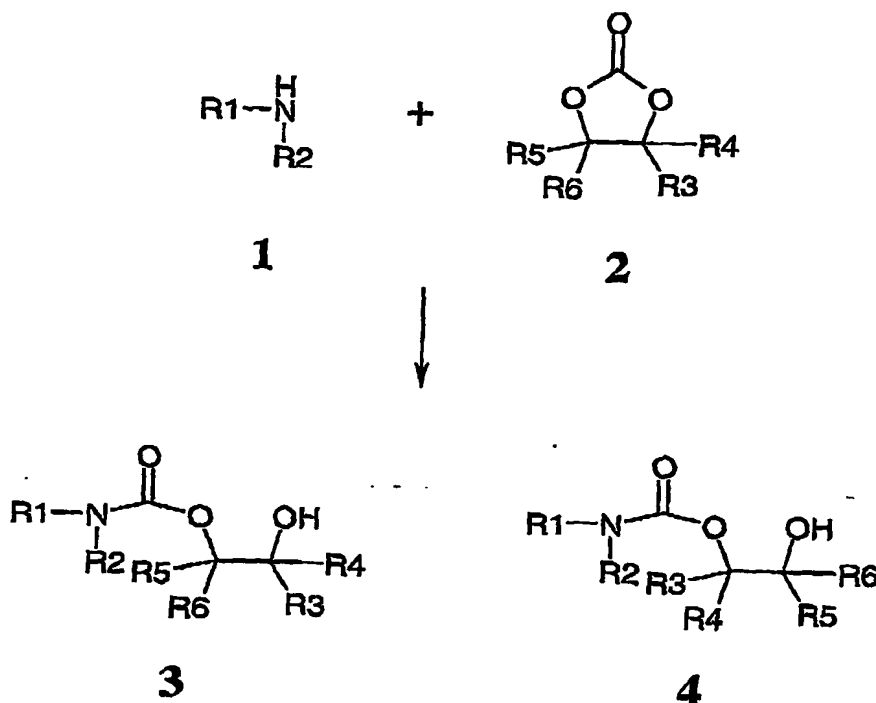
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR

Process using a cyclic carbonate reactant

The present invention relates to a process wherein a cyclic carbonate compound is reacted with a compound containing a nucleophilic function.

The reaction of a cyclic carbonate compound with a compound containing a nucleophilic group, especially an amine compound, is known. First publications on that subject date from late fifties early sixties: see for example US 2,802,022, US 2,935,494 and US 3,072,613.

When an amine compound (1) is reacted with a cyclic carbonate compound containing a 5-membered ring (1,3-dioxolan-2-one ring) (2), the product obtained is a betahydroxyurethane (3 and/or 4):



Urethane groups are useful in polymer preparation, such as polyurethanes, or other urethane-containing polymers.

Compared to ordinary urethane groups, betahydroxyurethane groups can provide desirable properties to the formed polymer, namely:

- the increased resistance towards hydrolysis (Figovski, O., Improving the protective properties of non metallic corrosion resistant materials and coatings. Journal of Medeleev Chemical Society, N.Y., USA 1988 Vol 33 No 3 .pp 31-36)
- more hydrophilic polymers

the extra functional groups make it possible to afterwards crosslink the polymer if desired

Another advantage of the reaction between amine and cyclic carbonate compounds is that it allows preparation of polyurethane polymers without isocyanate reactants. Such polymers are often called "non-isocyanate" polyurethane polymers. Although the use of diisocyanates for the synthesis of polyurethanes is widely accepted throughout the industry, there are some disadvantages connected with the NCO chemistry:

- diisocyanates are toxic and need special care while handled
- diisocyanates with a low vapour pressure can be absorbed easily by the human body (skin, eyes, lungs) and are to be considered as very hazardous chemicals
- their production involves phosgene while HCl is emitted: this process requires extreme safety measures
- because of the hydrogenation step and the consequent purification, aliphatic diisocyanates are expensive and often prevent the use of polyurethanes in a given application for economical reasons.

However, cyclic carbonates react relatively slowly with amines, particularly hindered primary or secondary amines and at ambient (about 25.degree. C.) temperatures. This slow reactivity has limited the usefulness of these types of reactions, for example in coatings which crosslink at ambient temperature. Therefore, means of speeding up such reactions is desired.

A great number of catalysts speeding up such reactions have been already described in literature:

US 5,055,542 issued in 1991 recommends the use of strongly basic compounds as catalysts for reaction including less reactive secondary amines. The patent reads: "Preferred catalysts are strongly basic amines, for example diazabicyclooctane (DABCO), guanidine etc. In addition, the so-called supranucleophilic catalysts, for example 4-pyrrolidinopyridine and poly(N,N-dialkylaminopyridine) are also suitable for this purpose." col 7, l. 59-63).

US 5,132,458 issued in 1992 says (col. 10, l. 8-23): "Suitable catalysts (...) are strongly basic compounds, such as quaternary ammonium compounds, for example alkyl-, aryl- and/or benzylammonium hydroxides and carbonates. Specific representatives of quaternary ammonium compounds in this case are alkylbenzyltrimethylammonium hydroxide (alkyl=C.sub.16-C.sub.22), benzyltrimethylammonium hydroxide and tetrabutylammonium hydroxide. Preferred catalysts are strongly basic amines, for example diazabicyclooctane (DABCO), guanidine, etc. .

So-called supranucleophilic catalysts, for example 4-pyrrolidinopyridine and poly(N,N-dialkylaminopyridine), are also suitable here; in this respect, cf. the article by R. A. Vaidya et al. in Polymer Preprints, Vol. 2 (1986), pp. 101-102. "

On page 3 of BE 1009543 published in 1997, the classic catalysts are again mentioned: tetramethylguanidine, dimethylaminopyridine, tetrabutylammoniumhydroxide and DABCO.

US 5,977,262, published in 1999, concerns "a process for the production of hydroxyurethanes by reacting a cyclic carbonate with a primary amine, wherein the improvement comprises, using as a catalyst a catalytically effective amount of a base whose conjugate acid has a pKa of about 11 or more." (col. 31-36).

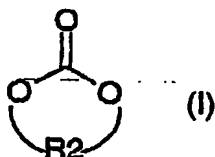
Catalysts shown in Table 1 are: "malononitrile anion, alkyl acetoacetate anion, N-methyl ethylcarbamate anion, methoxide, hydroxide, ethoxide, t-butoxide, N-alkylamide anion, anions of benzyl alcohols, anions of alkyl or aryl ketones, diphenylamine anion, triphenylmethoxide, N,N-bis(trimethylsilyl)amide anion". "Preferred bases are t-butoxide and N,N-bis(trimethylsilyl)amide (anion), and t-butoxide is especially preferred" (col. 2, l. 62-63).

The patent further mentions that the catalyst is preferably added in the form of a salt. The salt comprises as cation acting as counterion of the base anion "an alkali metal or ammonium salt, and more preferred it is a potassium salt." (col. 2, l. 63-67).

However, known catalysts are either not very effective (ammoniumsalts) and/or not suited for an industrial process (very strong bases such as potassium *tert*-butoxide). Moreover, some reagents (amines) are not compatible with the strong bases. On the other hand, without a catalyst the reaction takes several days.

The present invention provides a process of forming an organic compound, wherein

(a) a component (A) containing at least one cyclic carbonate group having the general formula (I):



wherein:

R2 represents a bivalent alkylene radical: $-(CR_3R_4)_p-$ with $p \geq 2$,

each R3 and R4 is independently chosen from: hydrogen, cycloaliphatic radical, aromatic radical, alkyl, alkylene or alkenylene C1-C10 chain which chain is linear or branched, contains from 0 to 8 ether bridges, and R3 and/or R4 may be substituted by an alkyl, alkenyl, hydroxyl group(s), or cyclic carbonate group of formula (I).

(b) is reacted with a component (B) containing at least one reactive nucleophilic function X which X is a primary amino or hydrazo ($-NH_2$), secondary amino or hydrazo ($-NH-$), thiol ($-SH$), and/or oxime ($-C(=NOH)-$)

(c) in presence of a catalyst comprising a lithium compound

(d) to form an organic compound (C) containing at least one unit of the general formula (II): $-X-CO-O-$.

Advantages obtainable by the claimed process include :

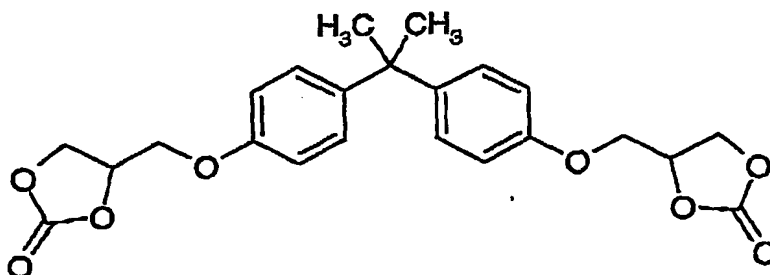
- An increase of reactionspeed during the synthesis of (poly)urethanes by reacting (poly)amines with (poly)cyclocarbonates (compared to prior art catalysts and to non-catalized reactions)
- Compatibility with many commercial amines such as JEFFAMINES (polyoxyalkyleneamines available from Huntsman Corp), in contrast with the preferred catalyst of the prior art patent US 5,977,262, which is a strong base: Potassium tertibutoxy (also called K t-butoxide).
- cheap, commercially available (poly)amines can be used for the synthesis of (poly)urethanes. These amines include JEFFAMINE, diethanolamine, piperazine....
- Because the reactionspeed is increased considerably even hindered primary and secondary amines can be used in the synthesis.
- Shorter reactiontimes also lead to an economical advantage.
- The new catalyst is a non-volatile and relatively safe reagent. For example LiBr has been used as a tranquilizer and Li_2CO_3 , LiOBenzoate have also been used as drugs.

In component (A), as specified above, R_3 and R_4 are chosen independently from each other. This means that R_3 and R_4 are chosen independently from each other on the same carbon as well as on different carbon atoms of the cycle.

The component (A) can comprise at least one carbonate cycle having 5, 6 or even more members in his ring. Preferably, the component (A) contains at least one 5-membered cyclic carbonate group. This means that $p=2$ in general formula (I). Such 5-membered cyclic carbonate compounds are very desirable because they can be easily prepared starting from cheap epoxides in a reaction with carbondioxide. A reaction of which is already known that it can be catalysed by a lithiumsalt : ref Kihara, N., Hara, N., Endo, T.; J. Org Chem., 1993, 58, 6198-6202.

For example component (A) can be: propylene carbonate, ethylene carbonate (formulas shown in the examples) and butylenecarbonate, glycerinecarbonate, allyloxymethylcarbonate.

More preferably, the component (A) contains at least two carbonate cycles. This permits to obtain dimers, oligomers or polymers, after rings openings. For example, component (A) is the chemical structure of a preferred biscarbonate : (made starting from the diglycidylether of bisphenol A)



Component (A) can be easily prepared by bubbling carbon dioxide through (poly-)epoxy compounds in the presence of a catalyst.

Examples of useful (poly)epoxide compounds include, without limitation, polyglycidyl ethers and esters, epoxy novolac resins, and epoxide-functional acrylics. In particular, the polyepoxide compound may be the polyglycidyl ether of aliphatic or aromatic polyols such as 1,4-butanediol, neopentyl glycol, cyclohexane dimethanol, diethylene glycol, polyethylene glycol, dipropylene glycol, polypropylene glycol, 2,2,4-trimethyl-1,3-pentanediol, 1,6-hexanediol, trimethylolpropane, trimethylolethane, glycerol, bisphenol A(4,4'-isopropylidenediphenol), hydroquinone, 4,4'-biphenol, 2,2'-biphenol, 4,4'-dihydroxybenzophenone, 1,5-dihydroxynaphthylene, novolac polyphenols, resorcinol, and similar compounds. In principle, the glycidyl ether of any polyol can be used. The polyepoxide compound is preferably a polyglycidyl ether of a polyphenol, and particularly preferably, it is the diglycidyl ether of bisphenol A. The polyepoxide compound could also be extended, for example by reaction of the diglycidyl ether of bisphenol A with a polyphenol such as bisphenol or with a polyamine such as those sold by BASF AG of Germany under the tradename POLYAMIN and under the tradename Jeffamine.RTM. by Huntsman Co. of Houston, Tex.

Preferably, the component (B) contains at least one nucleophilic function X which is an amino group. Preferably, component (B) is a monoamine, which can be chosen amongst cyclohexylamine, N-methylbutylamine, N-methylbenzylamine, piperidine, morpholine, benzylamine and derivatives thereof.

In other preferred embodiments of the invention, component (B) is a compound containing at least two amino groups (diamine). This permits to obtain dimers, oligomers and even polymers when reacted with a component (A) containing at least two linked carbonate rings.

Preferably, the diamine is an alkylamine, polyoxyalkyleneamine, ethanolamine, cyclohexylamine, piperazine and derivatives thereof.

Non limiting examples are:

- Diamines: Jeffamines (polyoxypropylenediamine such as D-230, D-400, D-2000....), 2-methyl-1,5-diaminopentane, 1,6-diamino-trimethylhexane, metaxylylenediamine (MXDA), 1,4-cyclohexanediamine, 1-amino-3-aminomethyl-3,5,5-trimethylcyclohexane (isophorone diamine or IPDA), bis-(4-aminocyclohexyl)-methane, bis-(4-amino-3-methylcyclohexyl)-methane, 1,3-diaminocyclohexane, 1,2-proylenediamine,
- Di-secondary amines: N,N'-dimethyl-1,3-propanediamine, N, N' -dimethylhexyl- 1,6-diamine, piperazine, 2,5-dimethylpiperazine.

The component (B) can also be chosen among hydrazo compounds such as:

Hydrazine, mono, di and tri-substituted hydrazines H_2N-NHR , H_2N-NR_2 , $RHN-NHR$, $RHN-NR_2$.

The lithium compound used as catalyst in the present invention is especially in form of a salt Li_mA comprising lithium as the cation (mLi^+) and an anion as counterion (A^{m-}). It is preferred that the lithium compound is lithium oxide (Li_2O), lithium hydroxide (LiOH), lithium carbonate (Li_2CO_3), methoxylithium (LiOCH_3), tertibutoxylithium (LiOtBu), lithium citrate, lithium chloride (LiCl), li-stearate ($\text{LiC}_{18}\text{H}_{35}\text{O}_2$), LiClO_4 , LiSO_4 , LiOAc , LiOOCPh and/or lithium bromide (LiBr). Especially preferred ones are Li_2O and LiBr . LiBr , Li_2CO_3 , Li citrate are advantageous because of their non-toxicity.

It was found that the reaction temperature is not critical and can be comprised between 0 and 120°C, preferably between 50 and 80°C.

Preferably the amount of cyclic carbonate groups contained in component (A) is in a $n:n+1$ molar ratio to the amount of nucleophilic groups in component (B).

Preferably the catalyst concentration is comprised between 0.01 and 5% by weight of the reacting mixture, preferably between 0.1 and 2% by weight of the reacting mixture. Such concentration was found sufficient for an effective speeding up of the reaction.

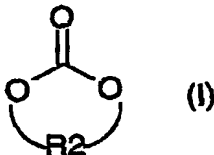
The reaction can be made with or without solvent. When a solvent is used, it is preferably chosen among alcohol, ether, ester, dimethylformamide and water.

Furthermore, component (A) containing at least one cyclic carbonate compound can be prepared by reaction of the corresponding epoxide compound with carbon dioxide (CO_2) in presence of a lithium compound as catalyst. This is particularly advantageous in industrial practice because the same catalyst can be used for successive reactions ("one-pot synthesis").

The invention also extends to polymeric composition containing a nonisocyanate polyurethane polymer comprising urethane functions $-\text{NCOO}-$ which contain ternary-substituted nitrogen and bear an hydroxy group in beta-position (betahydroxyurethane).

The invention further extends to the use of a lithium compound to catalyse a ring opening reaction wherein:

a component (A) containing at least one cyclic carbonate group having the general formula (I):



wherein:

R_2 represents a bivalent alkylene radical: $-(\text{CR}_3\text{R}_4)_p-$ with $p \geq 2$.

each R_3 and R_4 is independently chosen from: hydrogen, cycloaliphatic radical, aromatic radical, alkyl, alkylene or alkenylene C1-C10 chain which chain is linear or branched, contains from 0 to 8 ether bridges, and R_3 and/or R_4 may be substituted by an alkyl, alkenyl, hydroxyl group(s), or cyclic carbonate group of formula (I).

The invention will now be illustrated by examples.

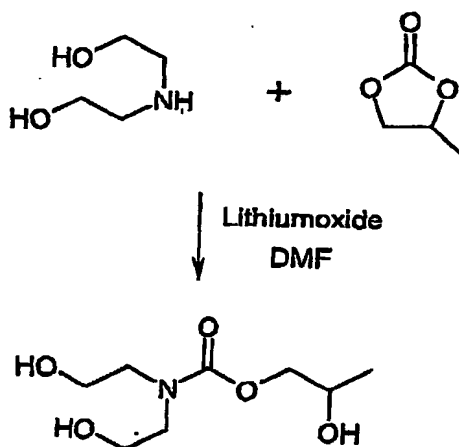
Examples 1 to 6 shows the reaction of diethanolamine and propylenecarbonate, without catalyst, with prior art catalyst and with catalyst according to the invention.

Example 7 to 10 shows the reaction of Jeffamine M600 with propylenecarbonate.

5 Example 11 is a comparative example showing one disadvantage of a prior art catalyst.

Example 12 shows the preparation of a tricarbamate by reaction of diethylenetriamine with ethylenecarbonate.

Example 1-6 (Reaction of diethanolamine and propylenecarbonate)



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To a suitable 3-neck flask equipped with a stirrer and a thermometer were added 105 grams (1 mole) of diethanolamine, 1200 ml of dimethylformamide and 204 grams (2 moles) of propylenecarbonate. The reaction was run at roomtemperature and followed by potentiometric titration of the amine. All examples were run in the same manner except for varying and/or amount of catalyst present. Results for the examples are shown in table 1.

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TABLE 1

Example	Catalyst ^a	Time (min) ^b				
		0	5	10	15	20
1	none	1.00	0.99	0.98	0.97	0.97
2	0.2 % BtMACl	1.00	0.98	0.97	0.96	0.96
3	2 % BtMACl	1.00	0.98	0.96	0.95	0.94
4	0.2 % BtMAOH	1.00	0.88	0.84	0.81	0.80
5	0.2% K tertiobutoxy	1.00	0.63	0.37	0.25	0.22
6	0.2% Li ₂ O	1.00	0.56	0.30	0.18	0.16

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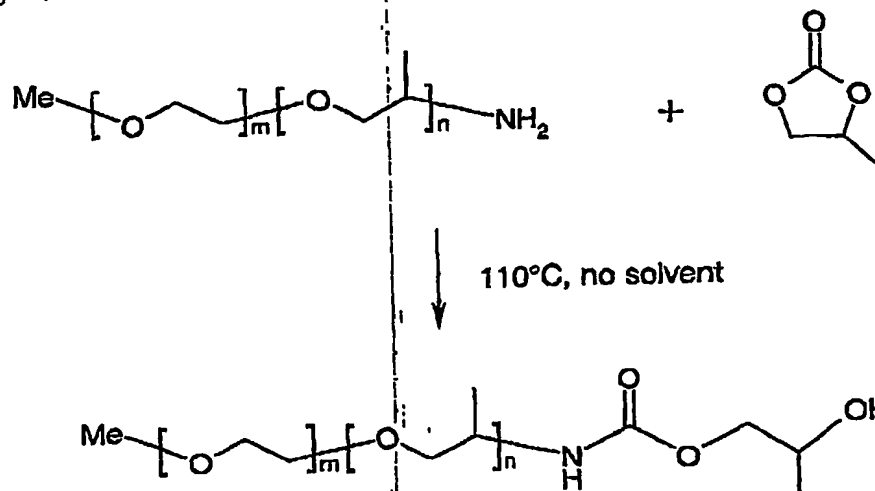
^b numbers given are relative (to time zero) amounts of amine
remaining at the given time
^a on total mass of sample

BtMACl = benzyltrimethylammonium chloride -

10 BtMAOH = benzyltrimethylammonium hydroxide

Example 7-10 (Reaction of JEFFAMINE M600 with propylenecarbonate)

Benzyltrimethylammoniumchloride = BtMACl.



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To a solution of 20 grams of JEFFAMINE RTM (Registered TradeMark) M600, (polyetheramine from Texaco, having an EO/PO ratio of 10/90 and molecular weight of 600 available from Huntsman Corp., Salt Lake City, Utah) was added 6.8 grams of propylenecarbonate and a catalyst if appropriate. The reaction was run at 110°C and followed by potentiometric titration of the amine. All examples were run in the same manner except for varying and/or amount of catalyst present. Results for the examples are shown in table 2.

TABLE 2

Example	Catalyst	Time (min) ^a				
		0	30	60	90	120
7	none	1.00	0.90	0.83	0.81	0.79
8	BtMACl ^b	1.00	0.87	0.79	0.72	0.68
9	BtMAOH ^b	1.00	0.81	0.70	0.60	0.53
10	LiBr ^b	1.00	0.73	0.56	0.45	0.39

^a numbers given are relative (to time zero) amounts of amine remaining at the given time

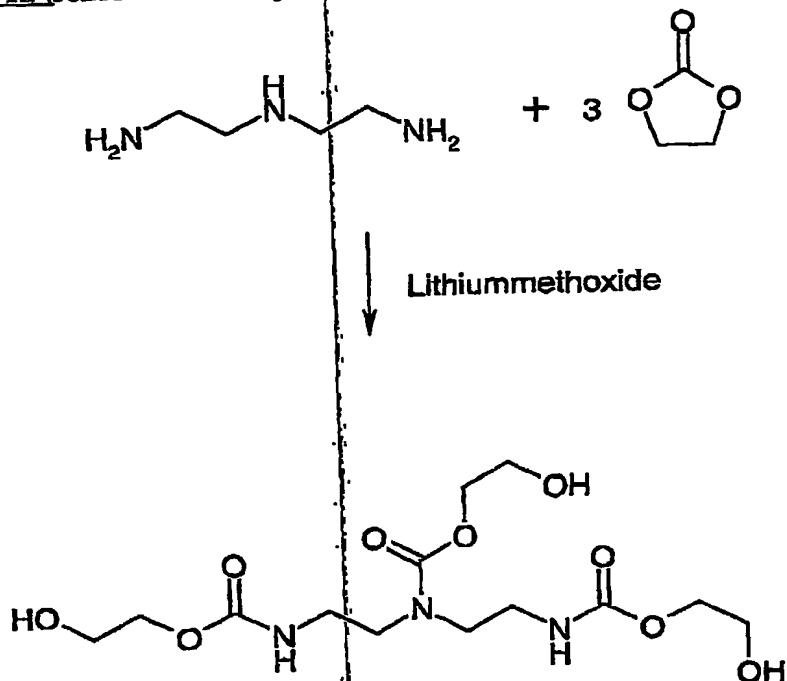
^b 3.5 % on total weight

Example 11 (comparative example with catalyst from US.5.977.262)

To a solution of 20 grams of JEFFAMINE RTM M600, (polyetheramine from Texaco, having an EO/PO ratio of 90/10 and molecular weight of 600 sold by Huntsman Corp., Salt Lake City, Utah), 3.4 grams of propylenecarbonate and 100 mg IRGANOX 1010 RTM of Ciba, Basel, Switzerland) is added 500 mg potassium *tert*-butoxide as a catalyst.

After a very short time the reaction mixture turns dark brown.

Example 12 (reaction of diethylene triamine with ethylenecarbonate) :



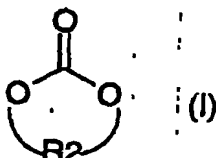
To a suitable 3-neck flask equipped with a stirrer and a thermometer were added 103 grams (1 mole) of diethylenetriamine and 264 grams (3 moles) of ethylene carbonate. At the completion of the ethylene carbonate addition the reaction mixture was allowed to react for several hours at 65°C. The yellow product was characterized by I.R. and potentiometric titration to be mainly tris(2-hydroxyethyl)iminodiethylene triscarbamate.

In the absence of a catalyst, the secondary amine diethylenetriamine is unreactive towards cyclic carbonates.

CLAIMS:

1. Process of forming an organic compound, wherein

(a) a component (A) containing at least one cyclic carbonate group having the general formula (I):



wherein:

R2 represents a bivalent alkylene radical: $-(CR_3R_4)_p-$ with $p \geq 2$,

each R3 and R4 is independently chosen from: hydrogen, cycloaliphatic radical, aromatic radical, alkyl, alkylene or alkenylene C1-C10 chain which chain is linear or branched, contains from 0 to 8 ether bridges, and R3 and/or R4 may be substituted by an alkyl, alkenyl, hydroxyl group(s), or cyclic carbonate group of formula (I),

(b) is reacted with a component (B) containing at least one reactive nucleophilic function X which X is a primary amino or hydrazo ($-NH_2$), secondary amino or hydrazo ($-NH-$), thiol ($-SH$), and/or oxime ($-C(=NOH)-$)

(c) in presence of a catalyst comprising a lithium compound

(d) to form an organic compound (C) containing at least one unit of the general formula (II):



2. Process according to claim 1, wherein component (A) contains at least one 5-membered cyclic carbonate group ($p=2$ in general formula (I)).

3. Process according to claim 1 or 2, wherein component (A) contains at least two carbonate cycles.

4. Process according to any preceding claim, wherein component (B) contains at least one nucleophilic function X which is an amino group.

5. Process according to claim 4, wherein component (B) is a monoamine.

6. Process according to claim 5, wherein component (B) is a monoamine chosen amongst cyclohexylamine, N-methylbutylamine, N-methylbenzylamine, piperidine, morpholine, benzylamine and derivatives thereof.

7. Process according to claim 4, wherein component (B) contains at least two amino groups (diamine).

8. Process according to claim 7, wherein component (B) is a diamine chosen amongst: alkylamine, polyoxyalkyleneamine, ethanolamine, cyclohexylamine, piperazine and derivatives thereof.

9. Process according to any preceding claim, wherein the lithium compound is lithium oxide (Li_2O), lithium hydroxide (LiOH), lithium carbonate (Li_2CO_3), methoxylithium (LiOCH_3), tertbutoxylithium (LiOtBu), lithium citrate, lithium chloride (LiCl) + Li-stearate ($\text{LiC}_{18}\text{H}_{35}\text{O}_2$), LiClO_4 , LiSO_4 , LiOAc , LiOOCPh and/or lithium bromide (LiBr).
10. Process according to any preceding claim, wherein the reaction temperature is comprised between 0 and 120°C, preferably 50 to 80°C.
11. Process according to any preceding claim, wherein the amount of cyclic carbonate groups contained in component (A) is in a n:n+1 molar ratio to the amount of nucleophilic groups in component (B).
12. Process according to any preceding claim, wherein the catalyst concentration is comprised between 0.01 and 5% by weight of the reacting mixture.
13. Process according to claim 12, wherein the catalyst concentration is comprised between 0.1 and 2% by weight of the reacting mixture.
14. Process according to any preceding claim, wherein the reaction is made in a solvent chosen among: alcohol, ether, ester, dimethylformamide, and water.
15. Process according to any preceding claim, wherein component (A) containing at least one cyclic carbonate compound is prepared by reaction of the corresponding epoxide compound with carbon dioxide (CO_2) in presence of a lithium compound as catalyst.
16. Use of a lithium compound to catalyze a ring opening reaction wherein:
a component (A) containing at least one cyclic carbonate group having the general formula (I):



wherein:

R_2 represents a bivalent alkylene radical: $-(\text{CR}_3\text{R}_4)_p-$ with $p \geq 2$,

each R_3 and R_4 is independently chosen from: hydrogen, cycloaliphatic radical, aromatic radical, alkyl, alkylene or alkenylene C1-C10 chain which chain is linear or branched, contains from 0 to 8 ether bridges, and R_3 and/or R_4 may be substituted by an alkyl, alkenyl, hydroxyl group(s), or cyclic carbonate group of formula (I),

is reacted with a component (B) containing at least one reactive nucleophilic function X which X is a primary amino or hydrazo ($-\text{NH}_2$), secondary amino or hydrazo ($-\text{NH}-$), thiol ($-\text{SH}$), and/or oxime ($-\text{C}(=\text{NOH})-$)

to form an organic compound (C) containing at least one unit of the general formula (II):
 $-\text{X}-\text{CO}-\text{O}-$.

ABSTRACT

The present invention relates to a process wherein a cyclic carbonate compound is reacted with a compound containing a nucleophilic group, especially an amine group.

Such reactions permits to obtain urethane groups useful in polymer preparation, such as polyurethanes, or other urethane-containing polymers.

The process is carried out in presence of a catalyst comprising a lithium compound, for example Li_2O or LiBr .

Such catalyst permits to speed up the reaction and is compatible with many commercial reactants.